

## Application of 2D NMR experiments for identification of alkyl 5-nitro-7,12-dioxo-7,12-dihydroindeno[1,2-a]fluorene-6-carboxylates

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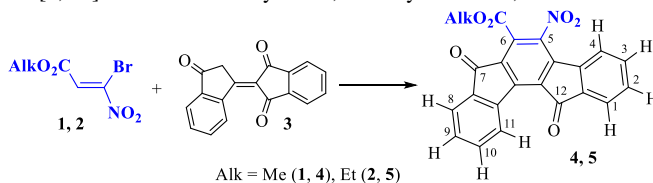
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The interaction of alkyl 3-bromo-3-nitroacrylates **1**, **2** we have studied with the original representative of cyclic CH acids - bindone ([1,2'-biindenylidene]-1',3,3'(2H)-trione) **3** – led to the preparation of previously unknown alkyl 5-nitro-7,12-dioxo-7,12-dihydroindeno[1,2-a]fluorene-6-carboxylates **4**, **5** with yields of 60, 90%.



In the <sup>1</sup>H NMR spectra of synthesized polyaromatic products **4**, **5**, proton signals of three isolated spin systems (an alkoxy-carbonyl group and two 1,2-disubstituted benzene rings) are observed, and the aromatic systems partially overlap with their signals at 7.53 (2H) and 7.62 (2H) m.d. (Fig. 1).

The study of compound **5** by <sup>1</sup>H-<sup>1</sup>H *J*-COSY NMR spectroscopy showed that the multiplet at 7.53 m.d. is formed by two triplet signals, and the multiplet at 7.62 m.d. is formed by a doublet and a triplet (Fig. 2). One should note the presence of two additional (symmetrical) signals (marked in red) in the <sup>1</sup>H-<sup>1</sup>H *J*-COZY spectrum in the region of two overlapping triplet signals (*t+t*), which, apparently, is a consequence of the strong coupling in the system of three proton signals at 9.05 d, 7.69 t, 7.53 m (ABX system), which manifests itself in such an unexpected way in this

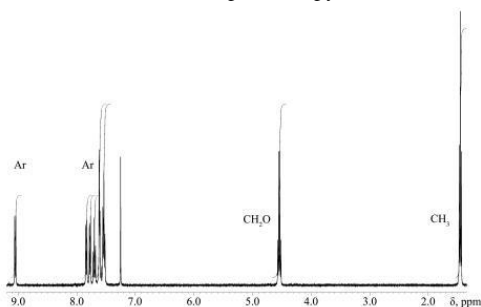


Figure 1. <sup>1</sup>H NMR spectrum of ethyl 5-nitro-7,12-dioxo-7,12-dihydroindeno[1,2-a]fluorene-6-carboxylate **5**

experiment.

The study of the same compound **5** by the  $^1\text{H}$ - $^1\text{H}$  dqf-COSY NMR spectroscopy allowed us to hypothesize that the observed signals belong to the corresponding protons in the structure of the molecule (Fig. 3). In the  $^1\text{H}$  NMR spectrum, a doublet at 9.05 m.d. can be attributed to the proton  $\text{H}^{11}$ , which is under the deshielding effect of the anisotropy of the neighboring carbonyl group ( $\text{C}^{12}=\text{O}$ ). Consequently, the cross peaks observed in the  $^1\text{H}$ - $^1\text{H}$  dqf-COSY spectrum relate to proton signals: 7.83 d ( $\text{H}^1$ ), 7.77 d ( $\text{H}^8$ ), 7.69 t ( $\text{H}^{10}$ ), 7.62 m ( $\text{H}^3$  and  $\text{H}^4$ ), 7.53 m ( $\text{H}^2$  and  $\text{H}^9$ ), 4.54 q ( $\text{CH}_2\text{O}$ ) and 1.45 t ( $\text{CH}_3$ ).

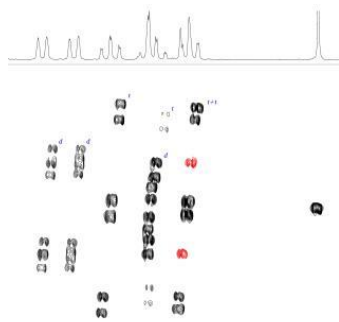


Figure 2. The fragment of  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of compound **5**.

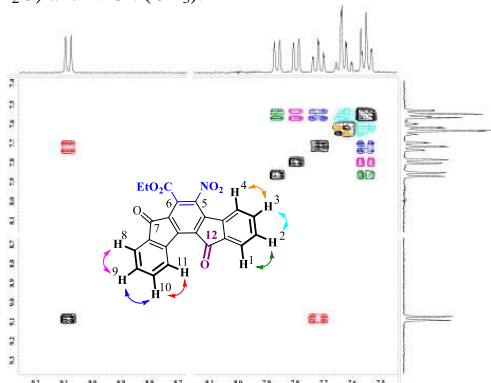


Figure 3. The fragment of  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of compound **5**

Our accepted assignment of proton signals correlates with the results of X-ray diffraction analysis performed for compound **4**. Thus, proton  $\text{H}^{11}$  is located near the carbonyl group ( $\text{C}^{12}=\text{O}$ ), falls into its deshielding region and undergoes a shift to a low field compared to other protons. At the same time, the proton  $\text{H}^4$  is located near the nitro group, which is removed from the plane of the cycle and cannot show a deshielding effect to it.

The studies were carried out at the Central Collective Use Center at the Faculty of Chemistry of the Herzen State Pedagogical University of Russia on the Jeol ECX-400A spectrometer (Royal probe) with an operating frequency of 399.78 ( $^1\text{H}$ ), 100.53 ( $^{13}\text{C}$ ) MHz at standard experimental settings, using the solvent signal as an internal standard.

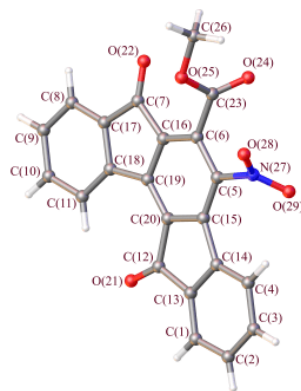


Figure 4. X-ray diffraction analysis of compound **4**

## Acknowledgements

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